

A Dinuclear Dysprosium-2-quinolinecarboxylate-1, 10-Phenanthroline Compound: Crystal Structure and Magnetism

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ABSTRACT A dinuclear dysprosium(III) compound, $[\text{Dy}_2(\mu_2\text{-OH})_2(\text{QLC})_4(1,10\text{-phen})_2] \cdot 4\text{H}_2\text{O}$ (**1**) ($\text{QLC}^- = 2\text{-quinolinecarboxylate}$ and $1,10\text{-phen} = 1,10\text{-phenanthroline}$), was synthesized and structurally and magnetically characterized. Compound **1** crystallizes in triclinic system, space group $P\bar{1}$ with $a = 10.9439(3)$, $b = 11.2823(3)$, $c = 12.2323(4)$ Å, $\alpha = 107.446(3)^\circ$, $\beta = 91.700(3)^\circ$, $\gamma = 91.511(2)^\circ$, $V = 1439.25(8)$ Å³, $Z = 1$, $\text{C}_{64}\text{H}_{50}\text{N}_8\text{O}_{14}\text{Dy}_2$, $M_r = 1480.12$, $D_c = 1.708$ g/cm³, $\mu = 2.653$ mm⁻¹ and $F(000) = 734$. The final $R = 0.0366$ and $wR = 0.0736$ for 5816 observed reflections with $I > 2\sigma(I)$. Compound **1** contains the mononuclear $[\text{Dy}(\text{QLC})_2(1,10\text{-phen})]$ subunit formed from one 1,10-phen and two QLC^- ligands chelating Dy(III) ion. Two mononuclear $[\text{Dy}(\text{QLC})_2(1,10\text{-phen})]$ subunits are bridged by a pair of $\mu_2\text{-OH}$ groups to give a centrosymmetric dinuclear $[\text{Dy}_2(\mu_2\text{-OH})_2(\text{QLC})_4(1,10\text{-phen})_2]$ with each Dy(III) ion being eight-coordinated. Detailed susceptibility measurements revealed that compound **1** does not show slow magnetic relaxation under zero direct-current field but exhibits field-induced slow magnetic relaxation under 2 kOe applied field.

Keywords: dinuclear Dy(III) compound; 2-quinolinecarboxylate; slow magnetic relaxation; crystal structure; DOI: 10.14102/j.cnki.0254-5861.2011-1733

1 INTRODUCTION

Many researches focus on the synthesis and studies of single-molecule magnets (SMMs) in the past two decades because of their potential applications in ultra-high density information storage and molecular spintronics^[1-4]. As the lanthanide ions have many electrons in the f orbits and a strong spin-orbital coupling effect, they are very appealing candidates for constructing SMMs. Thus, a large number of lanthanide-based SMMs have been reported recently^[5-8]. Among these lanthanide ions, Dy(III), a late lanthanide ($4f^n$, $n > 7$) with

a large value of angular momentum, has a stronger magnetic anisotropy than the early lanthanides ($n < 7$)^[9]. In addition, the Dy(III) ion has an odd number of $4f$ electrons ($n = 9$) and is a Kramer ion with doubly-degenerate ground states^[10], which leads to a flood of interesting Dy-based SMMs, including mononuclear-Dy(III)^[11, 12], dinuclear Dy₂^[13-16] and multinuclear Dy(III) clusters^[17].

It has been reported that the magnetic relaxation of lanthanide ions is strongly influenced by the coordination environment around them^[18, 19]. Carboxylate group can form strong coordination bonds with lanthanide ions to provide a high affinity for oxygen donors, which makes them appropriate candidates for creating robust SMMs^[20]. Furthermore, lanthanide ions have large radii, high coordination numbers and variable geometries. The carboxylate-based ligand can provide diverse coordination modes due to its multi-coordination sites, which fit well with the flexible coordination geometries of lanthanide ions^[21]. In this study, the rigid ligand 2-quinolinecarboxylate (QLC⁻) with one N and two carboxylate O donors is selected for the construction of dysprosium(III) SMMs, and 1,10-phen is used as an ancillary capping ligand. The 1,10-phen with large skeleton serves as a chelating ligand to terminate the propagation of the Dy-2-quinolinecarboxylate linkage to the 1D polymeric chain. The centrosymmetric dinuclear compound is composed of two eight-coordinated Dy(III) ions. In compound **1**, each Dy(III) ion is chelated by two coordinated QLC⁻ ligands with one 1,10-phen acting as the terminal ligand. Two Dy(III) ions are bridged by a pair of μ_2 -OH groups to form the dinuclear [Dy₂(μ_2 -OH)₂(QLC)₄(1,10-phen)₂] unit. To our knowledge, only the dinuclear lanthanide-QLC compound, tetranuclear [Dy₄(QLC)₁₂(H₂O)₆] 4H₂O, and 1D chain structures of [Pr(QLC)₃(H₂O)]_n and [Dy(QLC)₃(H₂O)₂]_n have been reported^[22-25]. In these reported compounds, the lanthanide centers are bridged by the QLC⁻ ligand, which are different from the μ_2 -OH groups bridging Dy(III) centers in the dinuclear structure of **1**. Herein, we present its synthesis, crystal structure and magnetic properties.

2 EXPERIMENTAL

2.1 Materials and instruments

All chemicals were of reagent grade and used as commercially obtained. Elemental analyses were carried out on an Elementar Vario EL III analyzer and IR spectra (KBr pellets) were recorded on PerkinElmer Spectrum One. The thermogravimetric measurement was performed with a Netzsch STA449C apparatus under nitrogen atmosphere in the Al₂O₃ containers with a heating rate of 10 °C/min from 30 to 800 °C. Magnetic

measurements were carried out on a Quantum Design MPMS-XL5 SQUID magnetometer in the temperature range of 2~300 K. Diamagnetic corrections were estimated from Pascal's constants for all constituent atoms^[26].

2.2 Synthesis of the compound $[\text{Dy}_2(\mu_2\text{-OH})_2(\text{QLC})_4(1,10\text{-phen})_2] \cdot 4\text{H}_2\text{O}$ (**1**)

A mixture of Dy_2O_3 (0.0186 g, 0.05 mmol), 2-quinolinecarboxylic acid (0.0346 g, 0.2 mmol) and 1,10-phenanthroline (0.0198 g, 0.1 mmol) in 10 mL H_2O was sealed in a 25 mL Parr Teflon-lined stainless-steel vessel. The vessel was sealed and heated to 140 °C. This temperature was kept for 2 days and then the mixture was cooled naturally to form block colorless crystals of **1**. The crystalline product was dried at ambient temperature (yield: 53.1% on the basis of Dy). IR (KBr pellet, ν , cm^{-1}): 3453(s), 3061(m), 1735(w), 1699(w), 1626(s), 1593(s), 1577(m), 1561(w), 1550(m), 1518(w), 1466(m), 1428(w), 1410(s), 1386(m), 1377(m), 1345(w), 1302(w), 1267(w), 1216(w), 1181(w), 1149(w), 1103(w), 1049(w), 1019(w), 976(w), 960(w), 898(w), 880(w), 864(w), 847(w), 807(w), 785(w), 774(w), 743(w), 729(w), 669(w), 629(w), 598(w), 521(w), 499(w), 483(w), 450(w).

2.3 Single-crystal structure determination

A single crystal of **1** with dimensions of 0.09mm \times 0.06mm \times 0.05mm was selected and mounted on a glass fiber. Single-crystal X-ray diffraction data were collected on a Rigaku Oxford SuperNova Single Source diffractometer with an Eos detector and Mo- $K\alpha$ radiation ($\lambda = 0.71073$ Å). The software of CrysAlisPro Agilent Technologies was used for collecting the frames of data, indexing the reflections, and determining the lattice constants, absorption correction and data reduction^[27]. The structure was solved by direct methods and successive Fourier difference synthesis (SHELXT-2014)^[28], and refined by full-matrix least-squares method on F^2 (SHELXTL-2014)^[29]. The lattice water molecule (O_2W) is disordered over two positions with the occupancy of 0.649 and 0.351. All non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogen atoms attached to carbon atoms were assigned to calculated positions. Hydrogen atoms bound to oxygen atoms were located in difference Fourier map and refined isotropically with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{O})$ and O–H bond distance of 0.85 Å. Hydrogen atoms of the disordered O_2W could not be located. The R values are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. The final $R = 0.0366$ and $wR = 0.0736$ ($w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 0.6918P]$, where $P = (F_o^2 + 2F_c^2)/3$) for 5816 observed reflections. $(\Delta/\sigma)_{\text{max}} = 0.002$, $(\Delta\rho)_{\text{max}} = 1.628$ and $(\Delta\rho)_{\text{min}} = -0.790$ e/Å³. The largest residual peak is within 0.9 Å of the Dy(III) ion, which resulted from the smear effect of the lanthanide ion. The selected important bond parameters are listed in Table 1.

3 RESULTS AND DISCUSSION

3.1 Crystal structure description

Compound **1** features a centrosymmetric dinuclear structure with one Dy(III) ion, one hydroxyl group, two QLC[−] ligands, one 1,10-phen ligand and two solvent water molecules in the asymmetric unit. As shown in Fig. 1, the Dy(1) ion is eight-coordinated by three carboxylate oxygen atoms (O(2), O(4) and O(5)) and one nitrogen atom N(1) from two QLC[−] ligands, two nitrogen atoms from one 1,10-phen ligand, and two hydroxyl oxygen atoms (O(1) and O(1A)) (Fig. 2). The Dy–O and Dy–N bond distances range from 2.227(3) to 2.472(3) Å and 2.563(4) to 2.634(3) Å, respectively (Table 1). The two crystallographically independent QLC[−] ligands display two types of coordination modes. One binds a Dy(III) ion in a chelating mode via its carboxylate group; the other chelates a Dy(III) ion through its nitrogen and one carboxylate O atoms (Fig. 1). As depicted in Fig. 1, one 1,10-phen and two QLC[−] ligands simultaneously chelate a Dy(III) ion to give a mononuclear [Dy(QLC)₂(1,10-phen)] unit. Two [Dy(QLC)₂(1,10-phen)] subunits are bridged by a pair of μ_2 -OH groups to generate a centrosymmetric dinuclear [Dy₂(μ_2 -OH)₂(QLC)₄(1,10-phen)₂] unit with the Dy(1)··Dy(1A) distance of 3.664(2) Å and Dy(1)–O(1)–Dy(1A) angle of 109.92°. The intramolecular $\pi \cdots \pi$ interactions between aromatic rings of the QLC[−] ligands and 1,10-phen ligands are observed (Fig. 1) with the centroid-to-centroid distances of 3.7007(1), 3.7340(1), 3.7258(1) and 3.8942(1) Å and dihedral angles of 3° and 6°, respectively. In the crystal packing, the closest intermolecular Dy··Dy separation is 9.988 Å (Fig. 3). In addition, the intermolecular $\pi \cdots \pi$ interactions between aromatic rings of the QLC[−] ligands are observed having the centroid-to-centroid distances of 3.5000(1), 3.8092(1) and 3.6151(1) Å and dihedral angles of 3°, 2° and 0°, respectively. The O(1)W lattice water molecule bonds to the dinuclear molecule through the hydrogen bond between the water molecule and hydroxyl oxygen (Table 2). Finally, the hydrogen bonds between the lattice water molecules are observed in compound **1** (Table 2).

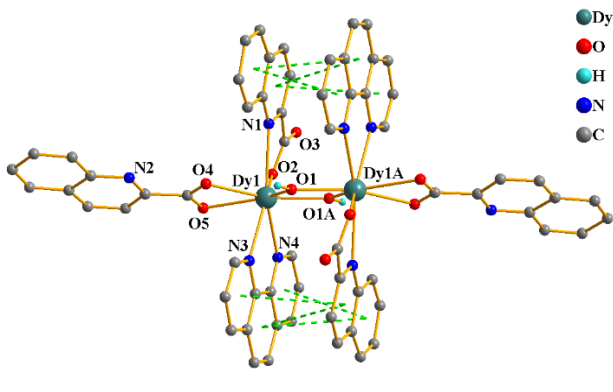


Fig. 1. Molecular structure of 1

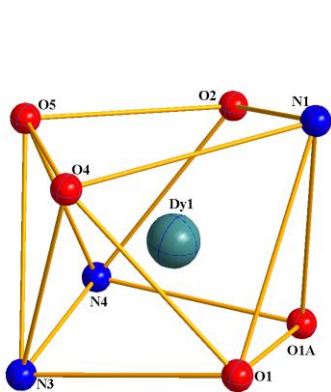


Fig. 2. Coordination polyhedron of the Dy(III) center in 1

Table 1. Selected Bond Lengths (Å) and Bond Angles (°) of Compound 1

Bond	Dist.	Bond	Dist.	Bond	Dist.
Dy(1)··Dy(1A)	3.664(1)	O(1)–Dy(1)–O(1A)	70.08(11)	O(1A)–Dy(1)–N(4)	78.33(10)
Dy(1)–O(1)	2.227(3)	O(1)–Dy(1)–O(4)	84.92(9)	O(4)–Dy(1)–O(5)	52.92(10)
Dy(1)–O(1A)	2.249(2)	O(1)–Dy(1)–N(1)	83.87(10)	O(4)–Dy(1)–N(1)	81.41(11)
Dy(1)–O(2)	2.291(3)	O(1)–Dy(1)–N(3)	78.78(11)	O(4)–Dy(1)–N(3)	76.50(12)
Dy(1)–O(4)	2.463(3)	O(2)–Dy(1)–O(5)	78.87(11)	O(5)–Dy(1)–N(3)	79.36(11)
Dy(1)–O(5)	2.472(3)	O(1)–Dy(1)–O(1A)	81.24(10)	O(5)–Dy(1)–N(4)	80.08(10)
Dy(1)–N(1)	2.634(3)	O(2)–Dy(1)–N(1)	65.65(12)	N(3)–Dy(1)–N(4)	63.77(12)
Dy(1)–N(3)	2.563(4)	O(2)–Dy(1)–N(4)	78.34(11)		
Dy(1)–N(4)	2.575(3)	O(1A)–Dy(1)–N(1)	88.33(10)		

Symmetry code: A : $-x + 2, -y + 1, -z + 1$

Table 2. Hydrogen Bonds of Compound 1 (Å and °)

D–H···A	d(D–H)	d(H···A)	d(D···A)	<DHA
O(1)–H(1)···O(1W)	0.85	2.17	3.003(6)	166.2
O(1W)–H(1WA)···O(2WA)	0.85	1.99	2.776(11)	153.4
O(1W)–H(1WB)···O(2WA) ^{#1}	0.85	2.28	3.130(12)	174.2

Symmetry code: #1: $-x + 2, -y + 2, -z + 1$

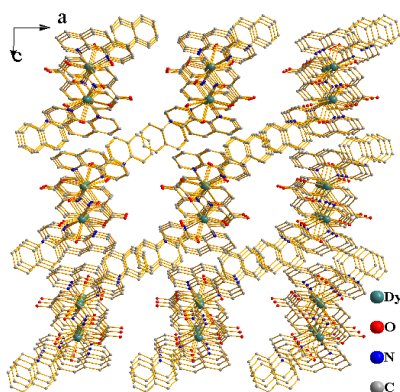


Fig. 3. View of the 3D frameworks of **1** along the *b* axis

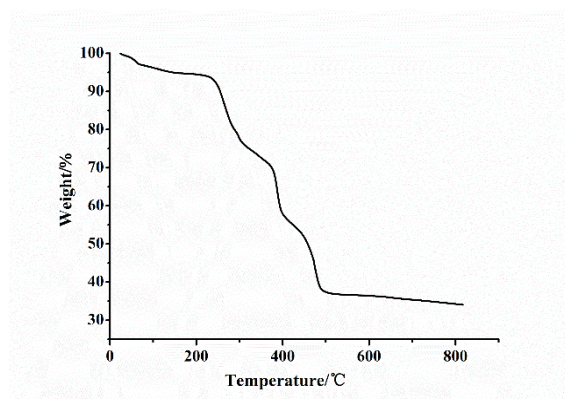


Fig. 4. TGA curve of compound **1**

3.2 IR spectra and TG analysis

The IR spectrum of compound **1** exhibits a broad absorption centered at 3453 cm^{-1} , which belongs to the O–H stretching vibrations of hydroxyl groups and water molecules. The strong bands at 1626 and 1593 cm^{-1} belong to the asymmetric stretching vibrations of the carboxylate group. The symmetric stretching vibrations of the carboxylate group can be observed at 1410 and 1386 cm^{-1} . The thermogravimetric analysis (TGA) curve of **1** is shown in Fig. 4. The TGA curve shows the first weight loss between 30 to $150\text{ }^{\circ}\text{C}$, which is attributed to the removal of solvent water molecules (observed 5.11% , calculated 4.86%). The combustion of the organic ligands starts at $230\text{ }^{\circ}\text{C}$.

3.4 Magnetic properties

Direct-current (dc) magnetic susceptibilities of **1** were collected under an applied magnetic field of 1 kOe in the temperature range of $300\sim 2\text{ K}$. The magnetic properties of **1** in the form of $\chi_{\text{M}}T$ versus T , where χ_{M} is the molar magnetic susceptibility per dinuclear molecular unit, are shown in Fig. 5. The $\chi_{\text{M}}T$ value is $28.29\text{ cm}^3\text{ K mol}^{-1}$ at 300 K , which is consistent with the expected value of two uncoupled Dy(III) ions in the $^6H_{15/2}$ ground state ($S = 5/2$, $L = 5$, $g = 4/3$, and $C = 14.17\text{ cm}^3\text{ K mol}^{-1}$). As the temperature lowered, the

$\chi_M T$ product increases gradually to a maximum value of $31.02 \text{ cm}^3 \text{ K mol}^{-1}$ at 44 K. As the temperature further lowered, $\chi_M T$ product decreases sharply to a minimum value of $22.58 \text{ cm}^3 \text{ K mol}^{-1}$ at 2 K (Fig. 5). A protuberance around 44 K in the $\chi_M T$ versus T curve indicates the presence of intramolecular ferromagnetic interaction between the Dy(III) ions within the dimeric unit. Such kind of interaction is strong enough to compensate the decrease of $\chi_M T$ resulted from the depopulated Stark states. However, this kind of intramolecular ferromagnetic interaction at higher temperature is rarely observed for lanthanide compounds, because it is generally masked by the thermal population of low-lying excited states as well as strong magnetic anisotropy for lanthanide ions^[30, 31]. The decrease of the $\chi_M T$ products at low temperature suggests that the intermolecular antiferromagnetic coupling starts to dominate the magnetic behavior for the ground states of **1**.

Field dependence of the magnetization at 2 K shows a rapid increase of the magnetization at low field followed by a slow linear increase at high field (Fig. 5 insert). The M value at 50 kOe is $16.8 N\beta$ at 2 K, which is much lower than the theoretic saturate value of $20 N\beta$, indicating a large magnetic anisotropy for Dy(III) ions. The small M value can be ascribed to the small total quantum number for Dy(III) ions produced by the depopulation of the Stark levels of the $^6H_{15/2}$ ground state under the ligand-field perturbation^[32]. In order to probe the slow magnetic relaxation behavior, the alternating-current (ac) magnetic susceptibility measurements are performed on **1**. Under a zero-dc field with an ac field of 2.5 Oe, no peak can be observed in the in-phase (χ') and out-of-phase (χ'') susceptibilities versus T curves in the high frequency of 997 Hz for **1** (Fig. 5b). Thus compound **1** shows no slow magnetic relaxation, which maybe results from zero-field quantum tunneling of the magnetization that is frequently associated with the lanthanide ions^[33]. To suppress the quantum tunneling of the magnetization, the dc field of 2 kOe is added. As shown in Fig. 5b, the peak with good shape is observed in the χ' and χ'' susceptibilities versus T curves with the frequency of 997 Hz (Fig. 5b). Thus the quantum tunneling of the magnetization of Dy(III) ions in compound **1** are suppressed. The temperature-dependences of χ' and χ'' susceptibilities under 2 kOe dc field are observed for **1** (Fig. 5b), suggesting that compound **1** exhibits a field-induced slow magnetic relaxation.

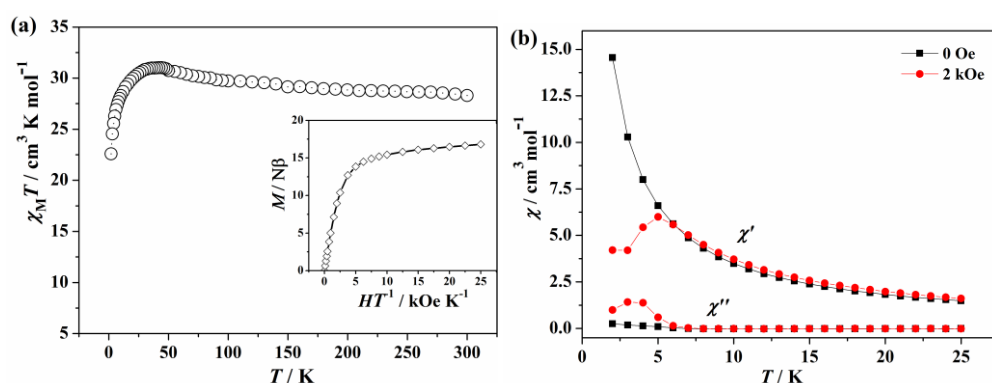


Fig. 5. (a) $\chi_M T$ versus T plot of **1** (insert: plot of magnetization versus applied field at 2 K)
(b) Temperature dependence of in-phase and out-of-phase ac susceptibility signals
under 997 Hz and zero and 2 kOe dc field for **1**

4 CONCLUSION

In conclusion, $[\text{Dy}_2(\mu_2\text{-OH})_2(\text{QLC})_4(1,10\text{-phen})_2] \cdot 4\text{H}_2\text{O}$ (**1**) constructed from the QLC^- and 1,10-phen mixed ligand has been reported. Compound **1** has mononuclear $[\text{Dy}(\text{QLC})_2(1,10\text{-phen})]$ subunits, which are bridged by $\mu_2\text{-OH}$ groups to give the whole dinuclear structure. Compound **1** shows no slow magnetic relaxation under zero-dc field, which may result from a fast magnetic relaxation, but it exhibits the field-induced slow magnetic relaxation.

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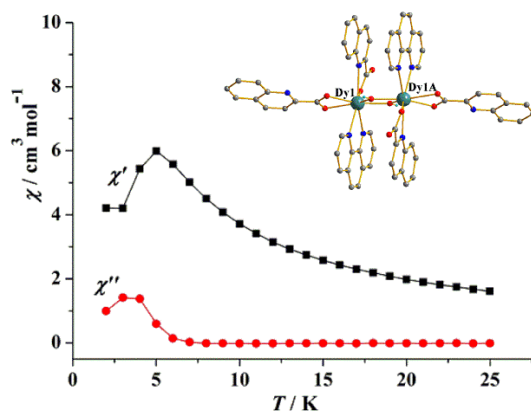
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A Dinuclear Dysprosium-2-quinolinecarboxylate-1,10-Phenanthroline

Compound: Crystal Structure and Magnetism

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A dinuclear Dy(III) compound, [Dy₂(μ_2 -OH)₂(QLC)₄(1,10-phen)₂] 4H₂O (**1**, QLC = 2-quinolinecarboxylate and 1,10-phen = 1,10-phenanthroline), was synthesized and characterized structurally and magnetically. Compound **1** shows field-induced slow magnetic relaxation.



中文题目和摘要:

一个双核镝-2-喹啉甲酸-1,10-邻菲罗啉化合物的 晶体结构和磁学性能^①

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摘要 本文报道一个双核镝化合物, $[\text{Dy}_2(\mu_2\text{-OH})_2(\text{QLC})_4(1,10\text{-phen})_2] \cdot 4\text{H}_2\text{O}(\mathbf{1})$ ($\text{QLC}^- = 2\text{-喹啉甲酸}$; $1,10\text{-phen} = 1,10\text{-邻菲罗啉}$)的合成, 晶体结构和磁学性能。化合物 **1** 结晶于三斜晶系的 $P-1$ 空间群, 其晶胞参数 $a = 10.9439(3)$, $b = 11.2823(3)$, $c = 12.2323(4)$ Å, $\alpha = 107.446(3)$, $\beta = 91.700(3)$, $\gamma = 91.511(2)^\circ$; $V = 1439.25(8)$ Å³, $Z = 1$, $\text{C}_{64}\text{H}_{50}\text{N}_8\text{O}_{14}\text{Dy}_2$, $M_r = 1480.12$, $D_c = 1.708$ g/cm³, $\mu = 2.653$ mm⁻¹, $F(000) = 734$ 。对于 5816 个 $I > 2\sigma(I)$ 的衍射点计算得到的 $R = 0.0366$ 和 $wR = 0.0736$ 。化合物 **1** 包含着由一个 1,10-邻菲罗啉和两个 2-喹啉甲酸螯合一个镝离子形成的单核的 $[\text{Dy}(\text{QLC})_2(1,10\text{-phen})]$ 单元。两个单核的 $[\text{Dy}(\text{QLC})_2(1,10\text{-phen})]$ 单元被一对羟基基团桥连形成了一个双核的 $[\text{Dy}_2(\mu_2\text{-OH})_2(\text{QLC})_4(1,10\text{-phen})_2]$ 结构。在这个化合物中, 镝离子是八配位的。磁学测试表明: 化合物 **1** 没有呈现出零场下的磁慢弛豫现象; 但在 2 kOe 外加磁场的作用下显示出了场诱导的磁慢弛豫现象。